Development of a formaldehyde exposure system for testing of residential monitoring badges for use by citizen scientists

THESIS

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Abstract

Formaldehyde is present in the air of nearly all indoor environments because it is utilized in many products present in homes such as pressed-wood structures, furniture and some clothing. Despite the health concerns and ubiquity in living spaces, the typical home occupant or business owner has no easy and affordable method to measure formaldehyde exposure levels. The overall goal of this work is to develop an in-home formaldehyde measurement system that can be easily used by citizen scientists and concerned citizens for less than $5 per measurement. The objective of the work in this thesis is to design a formaldehyde exposure unit for calibration of the system. Morphix Technologies currently sells colorimetric badges that detect formaldehyde in occupational settings. These badges are being modified and tested in order to improve usability in the residential environment and characterize the extent of color change relative to the formaldehyde dosage. This project details the use of an exposure chamber to expose the badges to several different concentrations of formaldehyde, ranging from 40-160 ppb. Through the use of a permeation tube system, as chemical reactions occur within the badge, it changes color and becomes darker. A SmartPhone App was created to measure the color change to allow for in-home formaldehyde readings. The blank samples resulted in 0.8 lightness as measured by Hue Saturation and Value (HSV) before and after exposure. As predicted, when exposed to 80 ppb and 160 ppb formaldehyde, the

value reduced to 0.775 and 0.750 lightness, respectively. The feasibility of testing formaldehyde must be improved in order to allow citizens across the entire population to measure their personal formaldehyde exposure levels and understand how these may be affecting their health. The SmartPhone App developed by this research will allow people to access this information readily and can empower citizen scientists to reduce their indoor exposure to this harmful contaminant.

Acknowledgments

I would like to thank Dr. Karen Dannemiller for supporting and advising me throughout this project. I am forever grateful Dr. Dannemiller saw the potential and allowed me this opportunity to explore the field of research and learn more about a specific aspect of my major. I would also like to thank Dr. Rongjun Qin for being a pivotal part of this research process. Along with Dr. Qin, I am exceedingly appreciative of Siyang Zhang who continuously worked with me to produce the most accurate results. The entire research team under Dr. Dannemiller, including Elizabeth Dorsey, Sarah Haines, Sam Cochran, Quentin Platt, Ashleigh Bope, and Ningling Zhu, were immensely supportive and offered any applicable advice. As always, I am forever grateful to my parents and family for supporting me throughout my research and college experience. Also, my research would not have been as successful without the financial assistance of the NSF award and research distinction scholarship. Lastly, I would like to thank The Ohio State University Engineering Program for providing me with an excellent education and endless opportunities to improve, broaden and continue my education.

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Introduction

Formaldehyde exposure is associated with eye, nose, and throat irritation, cancer and childhood asthma (Tillett, 2010). Associated cancers include lyphohematoepoietic cancer, sinonasal cancer, and nasopharyngeal cancer (2011, National Toxicology Program). When an individual is exposed to formaldehyde, irritation may occur based on the concentration of exposure. At about 50-1000 ppb ocular irritation occurs, between 100-1000 ppb nasal and throat irritation occurs, and at 5000-30,000 ppb a cough will develop (Broder et al., 1991).

Typically, formaldehyde is found in higher concentration in the home than outdoors (Khoder, 2000). The permissible exposure limit of formaldehyde (PEL) according to Occupational Safety and Health Administration (OSHA) is 750 ppb in occupational settings (Occupational Safety and Health Administration). However, health effects occur at much lower levels, and the NIOSH recommended exposure limit is 16 ppb. The typical exposure level for residential settings is much lower than the OSHA PEL but may be higher than the NIOSH REL. According to a study conducted in 1985, formaldehyde levels in 38 homes averaged 40 ppb. The maximum exposure level detected was around 140 ppb (Stock, 1985).

Formaldehyde is ubiquitous in the indoor environment because it is utilized in many products present in homes such as pressed-wood structures, furniture and some clothing (Tillett, 2010). The general population is exposed to formaldehyde on a daily basis since humans spend 86.9% of their life in environments that contain these products (Klepeis, 2001). In recent history there have been several events that resulted in increased public concern about formaldehyde. In the 1970s Urea Formaldehyde Foam Insulation became increasingly popular to improve energy conservation, which resulted in increased formaldehyde exposure in these homes (Williams et al, 1981). Formaldehyde was also in the news when Federal Emergency Management Agency trailers, which were supplied after Hurricane Katrina, contained high levels of this contaminant. In 2015 Lumber Liquidators was under scrutiny because its laminate flooring was found to contain elevated levels of formaldehyde. Due to these news stories and more, formaldehyde has become a contaminant of concern for the general public.

Despite the many health concerns surrounding formaldehyde, the typical home occupant or business owner has no easy and affordable method to measure formaldehyde exposure levels. The goal of this work is to develop an in-home formaldehyde measurement system that can be easily used by citizen scientists and concerned citizens for less than $5 per measurement. Morphix Technologies currently sells badges that detect formaldehyde in occupational settings by changing color as the surrounding pollutant concentration increases. These badges were modified and tested in order to improve sensitivity and characterize the extent of color change relative to the formaldehyde dosage. After several tests and programming efforts, the ultimate goal is a SmartPhone App that will measure the formaldehyde exposure based on digital images of the badge before and after exposure. This will allow for in-home measurements by citizen scientists and concerned citizens.

Approach

A. Kintek Ecoflex Permeation Tube System

We set up and used a KIN-TEK Ecoflex Permeation Tube System for formaldehyde exposure of the badges as seen in Figure 1. This system created a known concentration of formaldehyde to calibrate the badge color change. KIN-TEK, based in La Marque, Texas, specializes in calibration gas standards. In the Kintek Ecoflex oven, a permeation tube released a known amount of formaldehyde into the dilution gas. Valco Instruments Company Incorporated (VICI) supplied the “Formaldehyde-Para Perm Tube.” This company produces calibration gas generators, gas purifiers, detectors and several other air quality related devices. The concentration of formaldehyde in the outflow was manipulated by varying the flow rate entering the oven. These flow rates will be discussed in more detail in the next section.

Figure 1: EcoFlex^{TM} Permeation Tube System. Reproduced from (“Gas Standards and Vapour Generators”, 2014)

The gas mixture exits the oven through thin plastic tubing and into an exposure chamber. The exposure chamber consists of a glass container, a metal lid, a thin wire screen and a colorimetric badge. In order to allow the gas mixture to enter and escape from the chamber, two small holes were created in the top of the metal lid. To prevent the air from flowing directly across the badges, the inlet air enters from the uppermost hole. The lower hole is left unobstructed to allow the air to flow out of the chamber and escape into the fume hood. Also utilized to evenly divert the flow is a thin metal screen which ultimately slows and uniformly distributes the gas across the exposure area of each badge.

B. Flow Rates

The gas mixture is created by compressed air and a formaldehyde permeation tube. A gas regulator attached to the gas cylinder is used to vary the flow rate. This pressurized gas enters the oven where it is regulated and stabilizes around the selected flow rate.

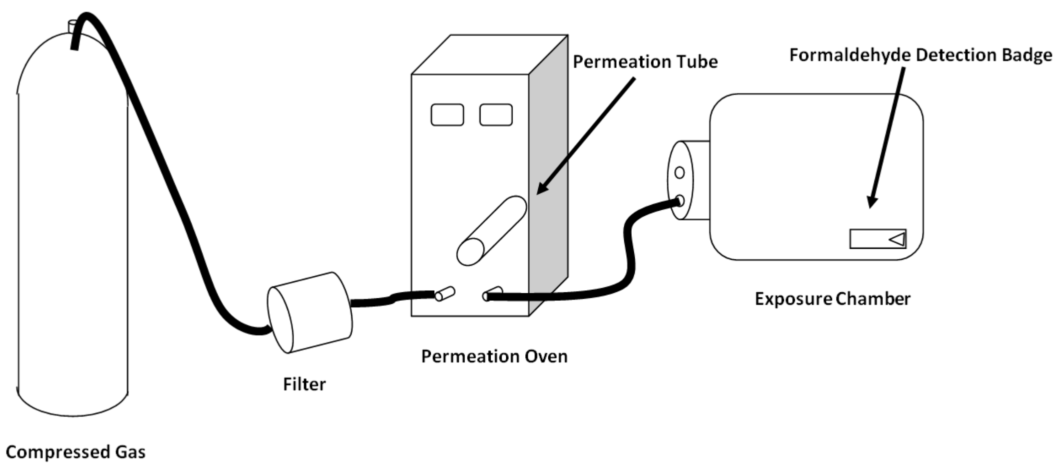

Figure 2: Permeation Oven and Exposure Chamber System

The flow rates were determined by the equation $F = \frac{P \cdot K}{C}$. F is the flow rate ($\frac{L}{min}$), P is the total permeation rate ($99\frac{ng}{min}$), K is the molar constant (0.814) and C is the concentration (ppb). The desired concentrations were varied in order to calculate the needed flow rate (Table 1).

Table 1: Formaldehyde Exposure Flow Variations

C	Concentration (ppb)	40	80	160
P	(Total) Permeation rate (ng/min)	99	99	99
K	(unitless)	0.814	0.814	0.814
F	Flow (Lpm)	2.015	1.007	0.504

As seen in Table 1 above, a lower flow is needed for higher concentrations. This relationship is due to the exposure time needed to adequately concentrate the air stream. A lower flow rate allows the compressed air a longer exposure period in the permeation tube and thus increases the concentration.

C. Badges and Alterations

The badge changes color and becomes darker as chemical reactions occur within the badge. We took digital images before and after exposure in order to compare the color alteration caused by the different formaldehyde doses. In the first version of the badges provided by Morphix Technologies the color change appeared in the shape of an "exclamation point" on the back of the badge as seen in Figure 3 and 4. The unexposed area was to remain unchanged in color. One limitation of these badges stemmed from the thin layer of plastic covering the exposure area. A glare from the overhead lighting was detected on some of the badge pictures.

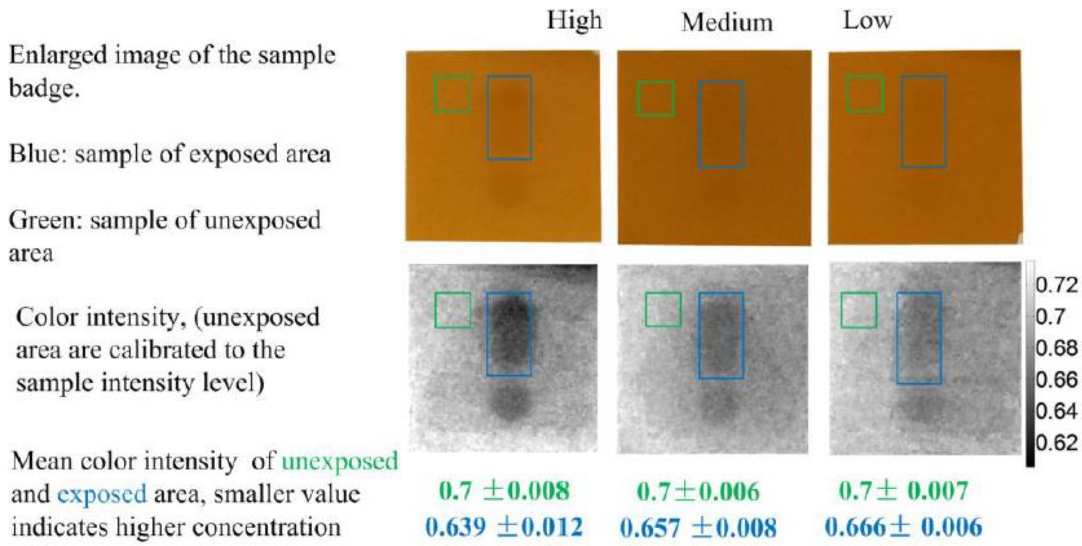

Figure 3: Example for high, medium and low exposure to formaldehyde of existing Morphix badges with (1)-shaped reaction area. Reproduced from SmART-Form NSF proposal with permission (Dannemiller et al, 2016).

After the original badges, the company then altered the badge to designate the bottom half to calibration (Figure 5). This part will not react with the formaldehyde and therefore remains yellow. These “Modified I” badges, were more sensitive to formaldehyde exposure. The change in color, before and after exposure was much more apparent and therefore easier to quantify. Instead of the color change occurring on the back surface of the badge, the Modified I badges exposure portion is on the front. Despite the greater sensitivity, the plastic covering was still present and therefore the glare limitation still existed.

Morphix also produced a Modified II badge (Figure 6) where the right half of the badge is designated for calibration and the plastic covering was removed. The chemical reaction is not limited to the "exclamation point" area but instead the whole left half of the badge. These badges were also more sensitive to formaldehyde than the original badges.

Figure 4: Morphix Technology Original Badge

Figure 5: Morphix Technology Modified I Badge

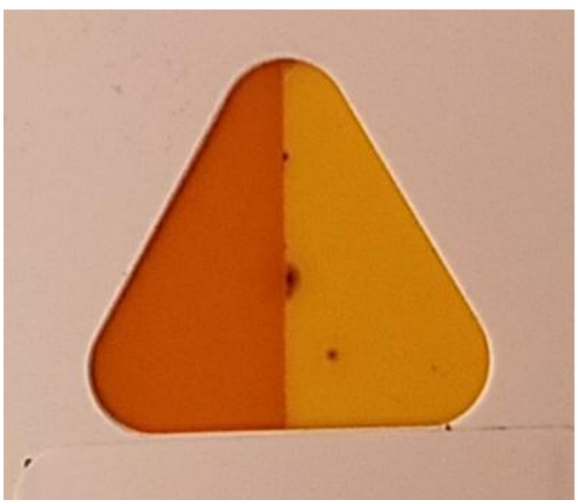

Figure 6: Morphix Technology Modified II Badge

D. Smartphone Application

In order to quantify the badge color change relative to the formaldehyde dosage, the SmartPhone App is being developed. There are several advantages to using SmartPhones to analyze the color change. For one, about 64% of all adults own a SmartPhone (Smith, 2015) . Lab on a Chip has also published studies on colorimetric sensors with SmartPhone detection. Our research is similar to this study because it uses images and predetermined calibration curves to quantify the contaminant concentration (Hong, 2014).

The SmartPhone App was created by graduate student, Siyang Zhang. When starting the App, the user is able to name the test and provide the relative location of the badge in the commercial or household setting. An initial picture of the badge is required for calibration. At the beginning of each test, the time is recorded and the user receives a notification when it is time to complete the test. To complete the test an after exposure picture is required. The time stamp of the two pictures is used for the amount of elapsed time from the start of sampling to the end.

The App was developed by using the badge images exposed to known formaldehyde concentrations. This App takes into account the pixel values of the color image and uses factors such as hue and lightness to measure the color variation. A model correlating the pixel values with the determined formaldehyde concentration provides the readings to the user on their SmartPhone device. Some parameters considered in this model are relative albedo and light conditions.

The variations of SmartPhone camera settings was a problem discovered in research. A problem that was discovered concerning the accuracy of the readings was varying SmartPhone camera settings. In order to prevent this variable from affecting the results, the App has programmed parameters that modify the user's camera settings to produce the optimal image. Another issue that was discovered was producing the clearest image possible for analysis. This was addressed by creating a triangle in the camera setting which indicates where the triangular portion of the badge should be captured (Figure 7). The App will also provide suggestions to users with high readings on potential methods to reduce their formaldehyde exposure.

Figure 7: Camera setting on Smartphone App

Results

Our initial experiment established the level of any background formaldehyde exposure that may be present in our system. Unaltered compressed air was run through the oven and over the badge. Similar experiments were conducted several times in order to ensure that the exposure system did not contain trace amounts of formaldehyde. Another air source was the "house air" that originates from the building. An experiment was conducted with the "house air" and compared to results utilizing the compressed air. The compressed gas proved to contain less contamination than the house air and was used throughout research (Table 2). In further research, to be consistent with the following results, the units for the negative control (HSV) will be converted to illumination.

Table 2: Blank Experiment Air Source Comparison

	Before Exposure (HSV)	**After Exposure (HSV)**
Compressed Air Blank	0.800	0.800
House Air Blank	0.800	0.790

After the negative control was established, the following experiments involved exposing the badges to trace levels of formaldehyde. The first experiment exposed the "Original" badges to 80 ppb at 1.007 LPM flow for 24 hours. Pictures were taken before and after exposure. Three badges were exposed in this experiment in order to test for any variation between the badges. Increasing the concentration of formaldehyde, the next exposure was 160 ppb at 0.504 LPM. The error in this experiment is relatively small (Figure 8)

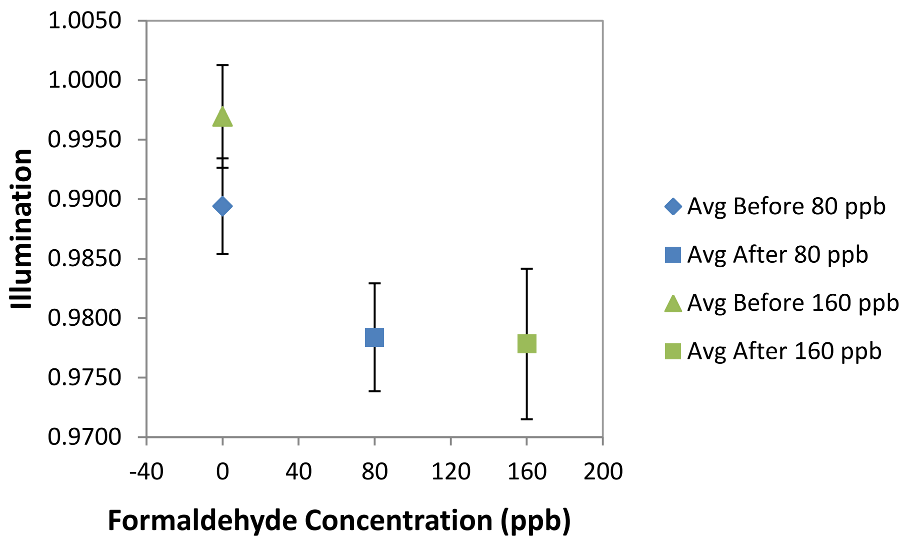

Figure 8: 80 ppb and 160 ppb, 24 hr Exposure Experiments

One of each of the Modified I and Modified II badges was exposed to 80 ppb for 24 hours. In order to improve the accuracy of the results, the before and after images were taken using the settings incorporated in SmartPhone App. Illustrated in Figure 8, these badges were noticeably more sensitive to the formaldehyde exposure.

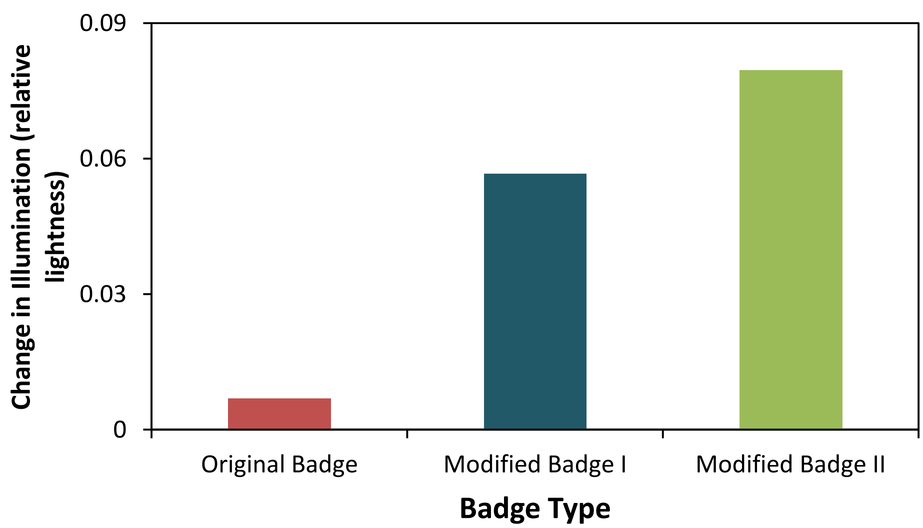

Figure 9: 80 ppb Badge 24 hour Sensitivity Comparison

Since the Modified I and Modified II badges were more sensitive, they were then exposed to 40 ppb. This experiment was run for 72 hours (Figure 10).

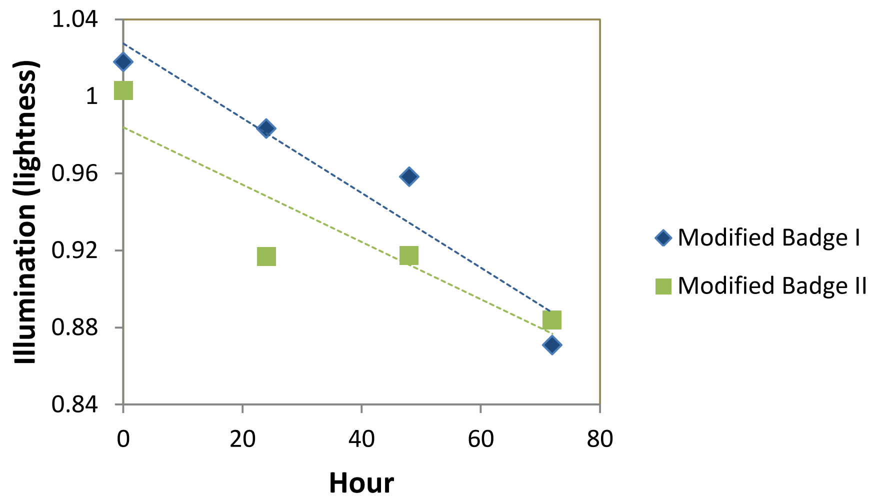

Figure 10: 72 hr, 40ppb, Modified Badges I & II Experiment

The next experiment was the same as the previous expect two Modified II badges were utilized and hourly pictures were taken. A picture of the badges was taken for 12 hours a day from 7 AM to 7 PM for 72 hours. As seen below, a calibration curve was created from the hourly data exhibiting an approximately linear relationship.

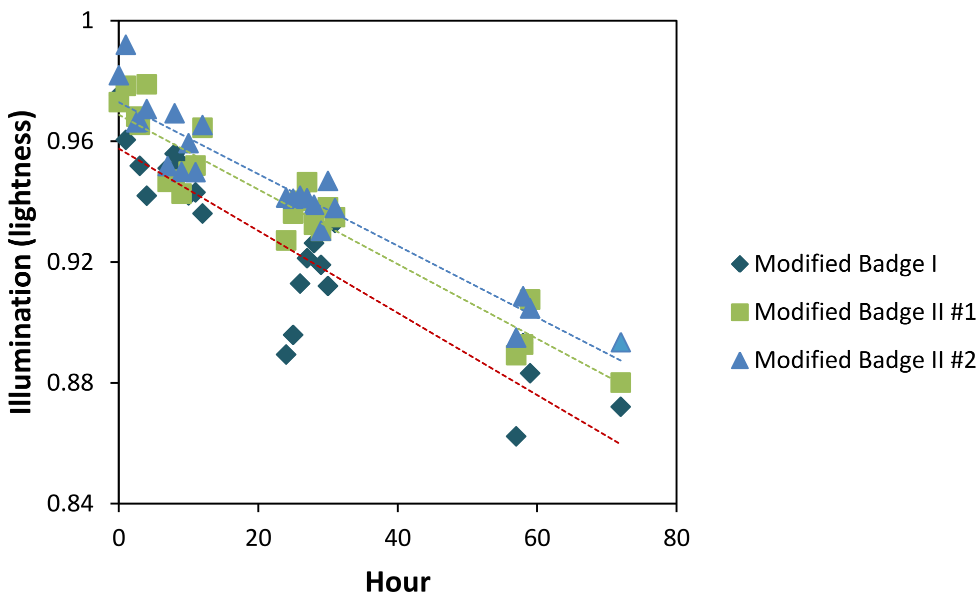

Figure 11: Results from Hourly Sampling Event at 40 ppb

Discussion

The focus of this research was to create a new innovative way to measure formaldehyde exposure. Many current formaldehyde measurement techniques are difficult, expensive, require expensive analytical instruments such as a gas chromotagraph/mass spectrometer, and are prone to contamination. The feasibility of testing formaldehyde must be improved in order to allow citizens across the entire population to measure their personal formaldehyde exposure levels and understand how these may be affecting their health. The SmartPhone App developed by this research will allow people to access this information readily.

This project provided the preliminary testing of Morphix's badges in order to measure the correlation between the different exposure concentrations and the resulting color change. We are working directly with Morphix to improve the badges such as the elimination of the badge discoloration. Sampling formaldehyde in living spaces will become a much more realistic option for concerned homeowners and business owners. One feature of the App allows participants to share their results with other users. Eventually, this will create a global database of formaldehyde exposure levels. The app will also provide mitigation suggestions to provide individuals with high exposure readings with options to reduce their exposure levels. This research not only improved the reliability and usability of the Morphix Technology badges, but also will improve public knowledge of formaldehyde in the environment, personal exposure levels, and indoor air quality standards.

Other formaldehyde measurement methods exist but are subject to limitations. One method used analyze formaldehyde in indoor are is photoaucoustic spectroscopy (PAS). This method is conducted by measuring the “sound” a sample produces resulting in a photocoustic spectrum. The limitations associated with this method include interference and high detection limits (Salthammer, 2010). Another system of formaldehyde measurement that has been tested is a portable instrument that involves gas collection, chromogenic reactions and scrubbers (Toda, 2005). This system is more accurate than the badges as it can detect to 0.08 ppb. The main limitation with this detection device is pricing. The system would be too costly for citizen scientists to use in residential settings.

The main findings of this research concern the badge sensitivity and relationship to formaldehyde exposure. The sensitivity analysis of each badge can be seen in Figure 9. Based on the improved sensitivity we suggest that Morphix produce the Modified II badges. These badges proved to be the easiest to analyze and therefore produced the most accurate results. From the 72 hour, hourly sampling experiment the color change appears to be linear with formaldehyde exposure. Therefore, over the period of exposure the color change should become more apparent.

Some limitations were able to be resolved by changing the App settings or modifying the badge as described above. However, some limitations in the research still exist. Discoloration was found on both the Modified I and Modified II badges. This discoloration limited the area of analysis for the App. The team is currently working with Morphix in order to eliminate the discoloration. Another limitation is the equal distribution of flow when exposing multiple badges. From the results, the middle badge consistently received the most exposure. This can be resolved by improved mixing within the exposure chamber. Additional limitations for future study include that there may some cross reactions with similar compounds such as acetaldehyde that need to be addressed. We also need to consider methods to further reduce the variability in the readings.

Conclusions

This work successfully established a formaldehyde exposure unit and tested colorimetric badges to calibrate them for late use by citizen scientists. Necessary modifications to the badges included removing the thin plastic covering over the exposure area, the addition of a calibration area, and increased sensitivity. These modifications improved the accuracy of the badges in detection of formaldehyde dosage. Overall, the formaldehyde badges and SmartPhone Application appear to work within the exposure range of the indoor environment.

Further research is planned in order to improve the accuracy and usability of the badges. BEESL (Building Energy and Environmental Systems Laboratory) validation testing will be conducted to ensure the accuracy of the badge readings. Community feedback will be gathered to test the usability of the SmartPhone App. Finally, a case study will be preformed to understand how the exposure kits in actual home environments and used by citizens. With this research and further studies, the consumer will receive the most accurate results to understand their personal exposure to formaldehyde. This work will empower citizen scientists and concerned citizens to measure their formaldehyde exposure.

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Appendix

Table 3: 24 hr, 80 ppb, Three Original Badge Experiment

	Before Exposure (HSI)	**After Exposure (HSI)**
Badge #1	0.9814	0.9855
Badge #2	0.9944	0.9700
Badge #3	0.9924	0.9797

Table 4: 24 hr, 160 ppb, Three Original Badge Experiment

	Before Exposure (HSI)	**After Exposure (HSI)**
Badge #1	0.9991	0.9662
Badge #2	0.9886	0.9879
Badge #3	1.0031	0.9793

Table 5: 24 hr, 80ppb, Modified Badges I & II Experiment

	Before Exposure (HSI)	**After Exposure (HSI)**
Modified Badge I	1.0164	0.9597
Modified Badge II	1.1309	1.0513

Table 6: 72 hr, 40ppb, Modified Badges I & II Experiment

	HSI	
Hour	**Modified I**	**Modified II**
0	1.0179	1.0031
24	0.9833	0.9168
36	0.9583	0.9175
72	0.8709	0.8838

Table 7: 72 hr, 40ppb, Modified Badges I & II, Hourly Sampling Experiment

	HSI		
Hour	**Modified I**	**Modified II #1**	**Modified II #2**
0	0.9753	0.973	0.9819
1	0.9605	0.9784	0.992
2.5	0.9668	0.9682	0.9663
3	0.9519	0.9655	0.9665
4	0.942	0.9789	0.9707
7	0.9511	0.9466	0.9518
8	0.9559	0.9473	0.9693
9	0.9526	0.9427	0.9499
10	0.9421	0.95	0.9594
11	0.9431	0.952	0.9498
12	0.9361	0.9645	0.9654
24	0.8894	0.9272	0.9414
25	0.8959	0.9361	0.941
26	0.9129	0.9403	0.942
27	0.9213	0.9465	0.9412
28	0.9263	0.9324	0.939
29	0.9191	0.9303	0.9304
30	0.9121	0.9382	0.9469
31	0.933	0.9349	0.9379
57	0.8623	0.8892	0.895
58	0.8932	0.8927	0.9087
59	0.8832	0.9076	0.9047
72	0.8721	0.8801	0.8935